

Surface stress of Ni adlayers on W(110): the critical role of the surface atomic structure

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Abstract. Puzzling trends in surface stress were reported experimentally for Ni/W(110) as a function of Ni coverage. In order to explain this behavior, we have performed a density-functional-theory study of the surface stress and atomic structure of the pseudomorphic and of several different possible 1×7 configurations for this system. For the 1×7 phase, we predict a different, more regular atomic structure than previously proposed based on surface x-ray diffraction. At the same time, we reproduce the unexpected experimental change of surface stress between the pseudomorphic and 1×7 configuration along the crystallographic surface direction which does not undergo density changes. We show that the observed behavior in the surface stress is dominated by the effect of a change in Ni adsorption/coordination sites on the W(110) surface.

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1. Introduction

The importance of surface stress has been demonstrated for many surface processes, such as nanopatterning, surface reconstruction, interfacial mixing, and segregation [1, 2, 3, 4, 5, 6, 7, 8, 9]. In spite of its importance, however, a general understanding of the key factors governing the dependence of surface stress on the atomic structure of the surface is still lacking. This applies, in particular, to the case of heteroepitaxy, and to the growth of metal adlayers on metal surfaces, where lattice mismatch is often assumed to be the prevailing factor controlling surface stress [10].

Specifically, in the case of metal adlayers on metal surfaces, puzzling changes in surface stress, as a function of adlayer coverage, have been observed experimentally [11, 12, 13, 14]. Such changes are at variance with predictions based on lattice misfit arguments and model elasticity theory [11, 12, 13, 14]. One interesting example is the Ni adlayer on W(110), whose surface stress was examined in some detail experimentally [13, 14]. In this system, the surface-stress changes along two orthogonal directions of the tungsten surface, $[1\bar{1}0]$ and $[001]$, were measured as a function of Ni coverage [13, 14]. With increasing coverage, Ni goes through a range of phases [15, 16], a pseudomorphic (PS) 1×1 configuration, 1×8 and 1×7 coincidence structures, and finally a fcc(111)-like Ni overlayer with Nishiyama-Wassermann orientation on W(110) [15]. The epitaxial strain of the Ni(111) layer is decreasing with increasing coverage, from $\sim 27\%$ in the PS to $\sim -1\%$ in the 1×7 structure along W $[001]$, while it remains constant ($\sim 4\%$) in these two phases along W $[1\bar{1}0]$. The atomic density is increasing to 9 Ni per 7 W atoms along $[001]$ in the 1×7 structure, whereas no change in periodicity relative to the PS configuration occurs in the perpendicular direction [17]. Interestingly, it was measured that the stress change between PS and 1×7 along $[1\bar{1}0]$ is considerably greater than the one along $[001]$, where actually a change of strain occurs. It remains unclear what are the microscopic changes in the Ni/W(110) atomic structure related to this surprising behaviour.

The structural properties of Ni/W(110) have been investigated experimentally by various techniques [15, 16, 18, 19, 20, 21, 17, 22, 23]. The types of reconstructions are known from low-energy electron diffraction (LEED) [15, 17] and scanning tunneling microscopy (STM) [16], but the actual details of the atomic structures are not well known or have large uncertainties. A model for the 1×7 coincidence structure has been proposed based on surface x-ray diffraction (SXRD) measurements [14]. It is characterized by distorted Ni hexagons and by a surprisingly large motion (up to 0.5 \AA) of the subsurface-layer W atoms. Such displacements of the W atoms were suggested to be responsible for the anomalous behaviour of the Ni/W stress [14]. However, because of the coexistence of various Ni phases at the deposition temperature used in Ref. [14], there is significant uncertainty on the structural details derived from the SXRD [14].

Ni/W is a prototype bimetallic system [15, 16, 18, 19, 20, 21, 17, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. Such systems are particularly interesting due to their catalytic properties [32, 33, 27, 28, 21, 29, 30, 31], which often closely depend on surface structural

changes. In addition, Ni has a very small atomic radius (the smallest of all fcc metals), so the study of its growth on bcc surfaces, such as the W surface, is especially helpful for understanding fcc/bcc metal interfaces [34, 15]. The Ni/W system has been studied amply also for its interesting magnetic properties [24, 35, 25, 26].

In this paper, we address the surface stress and atomic structure of the Ni/W 1×1 and 1×7 phases by means of first-principles density-functional-theory (DFT) calculations. In particular, we investigate the dependence of the surface stress on the atomic structure, with the aim of better understanding the key factors controlling the stress behaviour in this type of bimetallic systems. Ni/W(110) is an interesting case for this type of study as a surprising and unexplained stress change (related to unidentified structural modifications) between the two phases has been measured experimentally. For the 1×7 phase we predict a different, more regular atomic structure than the one proposed on the basis of the SXRD analysis [14]. The surface stresses we obtain for the theoretical lowest-energy 1×1 and 1×7 configurations account well for the stress behaviour observed experimentally. Moreover, the change in surface stress between the 1×1 and 1×7 structure is shown to be dominated by the effect of a change in the Ni adsorption/coordination sites on the W(110) surface. This is in contrast to the situations where surface stress is determined mostly by elastic strains or charge transfer, which can be excluded in this system.

2. Methods

The DFT calculations were performed using pseudopotentials and a plane-wave basis, as implemented in the PWscf code, a part of the Quantum ESPRESSO distribution [36]. The local-density approximation (LDA) in the Perdew-Zunger parametrization [37] was adopted for the exchange and correlation functional. To simulate surfaces with different adlayer configurations, we used a supercell method, for which we constructed an asymmetric slab with 1 Ni layer on 5 layers of W substrate (bottom 2 W layers were fixed) and 9 equivalent vacuum layers, both for relaxations and subsequent stress calculations. Laterally, we used 1×7 cell. Only for the calculation of the adsorption sites we used 15-layer asymmetric 1×1 slabs, in which 12 layers were allowed to relax.

Vanderbilt ultra-soft pseudopotentials [38] were generated from the $3d^9 4s^1$ atomic configuration of Ni and from the $5s^2 5p^6 5d^4 6s^2$ configuration of W. The core-cutoff radii for Ni were: $r_s = 2.0$ a.u. and $r_d = 1.6$ a.u., and for W: $r_{s,p} = 2.2$, $r_d = 2.4$ a.u. Our kinetic energy cutoff was 35 Ry for the wave functions and 350 Ry for the charge density. A $38 \times 38 \times 1$ k-point Monkhorst-Pack mesh [39] centered at Γ was used for the 1×1 surface unit cell and a grid of comparable density $24 \times 6 \times 1$ for the 1×7 surface unit cell. We employed a Gaussian level smearing of 0.01 Ry. The calculations were performed with the theoretical W lattice constant of 3.14 Å which is only 0.6 % different from the experimental lattice constant of 3.16 Å. The use of the theoretical equilibrium lattice constant ensures that no spurious stresses are present on the surface [40]. Total energy differences were converged to better than 0.1 meV. The forces in the 1×7

calculations, used as a criterion for the structural relaxation, were converged to better than 2 mRy/Å and the estimated uncertainties in the positions were 0.007 Å along $[1\bar{1}0]$ and 0.010 Å along $[001]$. For the clean W(110) and Ni/W(110) PS calculations, the forces were converged to better than 0.2 mRy/Å and we estimated the uncertainties in positions to be around 0.001 Å in both directions.

We also performed calculations for the clean Ni(111) surface (non magnetic) which were necessary for the interpretation of our results. For the calculation of the Ni(111) surface, we used our optimized lattice constant of 3.42 Å and a slab of 11 Ni layers. From our preliminary calculations we found the Ni PS layer on W(110) to be non magnetic; the initial ferromagnetic Ni/W(110) configuration converged into a non-magnetic structure. This is consistent with findings in [41] and [42]. Hence, in the remaining part of this work all calculations refer to non-magnetic configurations.

Surface stresses were computed using the analytical expression derived by Nielsen and Martin [40], based on the Hellmann-Feynman theorem. The surface stress uncertainty was estimated to be ~ 0.3 N/m on the basis of convergence tests regarding the wave-function and charge-density cutoffs, the number of k-points, and the number of vacuum layers [43]. As we used asymmetric slabs (with Ni on top and frozen W on the bottom), in order to obtain surface-stress values for the Ni-terminated surface, we subtracted the reference-surface stress of the frozen W surface.

3. Results and discussion

3.1. Pseudomorphic phase

The pseudomorphic Ni monolayer on W(110) may be viewed as a fcc-Ni(111) layer, oriented with the in-plane Ni $[1\bar{1}0]$ axis parallel to the W $[001]$ in-plane direction, and laterally stretched along the W $[001]$ and W $[1\bar{1}0]$ orthogonal directions. The Ni atoms can sit at or near any of the possible high-symmetry adsorption sites of W(110): “hollow” (H) in the central-symmetric position, in a perfect continuation of the W bulk lattice, “3-fold” (T) for which the Ni atoms are shifted along $[1\bar{1}0]$ to increase their coordination to the 3 nearest W neighbors, or “bridge” (B) where the Ni atoms are located midway between two W atoms along $[1\bar{1}1]$. The sites H, T and B are shown in Fig. 1a). A recent LEED I-V study [44] found that Ni atoms in the PS structure prefer to sit somewhere off the H site with a displacement toward the T-site. This is in apparent contrast to the case of the PS Fe on W(110), where the Fe atom has been reported to sit at the H site [45].

Table 1 collects our calculated data on energy differences and relaxed atomic structures corresponding to initial configurations with the Ni atom at the H, T and B sites. The relaxed T' structure, obtained starting from the Ni at the T site, has the lowest-energy, albeit with a very small energy difference with respect to the H site. This small energy difference and rather large displacement from the H site create a flat energy profile over a significant distance along $[1\bar{1}0]$ (H-T'). This energy profile is

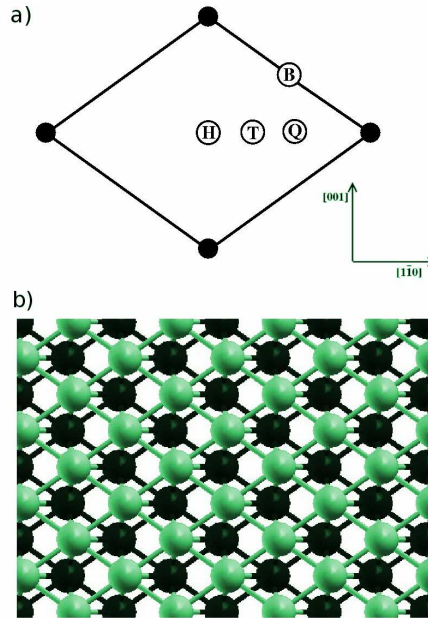


Figure 1. Possible adsorption sites for Ni/W(110) (a). T denotes 3-fold, H hollow, B bridge site and Q denotes the site at one quarter of the W-W distance along $[1\bar{1}0]$. Black circles denote underlying W atoms, while an open circle stands for Ni atom. Calculated pseudomorphic structure of Ni/W(110) (b). W atoms are shown in black and Ni atoms in green (grey).

likely to result in soft modes, which can persist also at higher temperatures. We note that the same relaxed T' structure is obtained starting from a configuration where the Ni is at the Q site, which is at $1/4$ of the W-W distance along $[1\bar{1}0]$ [Fig. 1 (a)] and from a lower-symmetry configuration where the Ni atom is located at an intermediate position between the H and B site. The B site is clearly very unfavorable (~ 0.36 eV per Ni surface atom higher than T'). Figure 1 b) shows the lowest-energy pseudomorphic structure (T'). The Ni is close to the H site, but displaced along $[1\bar{1}0]$ at slightly less than $1/2$ of the H-T distance. All results in Table 1 are for the 15-layer asymmetric slabs (the bottom 3 layers are fixed to the bulk positions, while the remaining 12 layers are allowed to relax). We note that the Δx displacements in Table 1 are given with respect to the bulk coordinates.

Our results are thus consistent with the slight displacement of the H site observed by LEED I-V. The T' site for Ni/W(110) may come as a surprise if one assumes a strong influence of the substrate in determining the adsorption site. Actually, for unreconstructed one-monolayer adsorbate surfaces it is often simply assumed that the adsorption will occur as a continuation of bulk. On the other hand, one can reason that Ni(111) has a hexagonal in-plane structure with a 3-fold coordination, which might

influence a shift away from the hollow site.

Table 1. Energy difference between the equilibrium pseudomorphic configurations obtained by structural relaxations starting from the Ni atom at the H, T and B adsorption sites, respectively. The relaxations of the interlayer distances ($\Delta d_{n,n+1}$) and, for the T' configuration, the displacements along $[1\bar{1}0]$ (Δx), relative to the ideal hollow site (or the ideal bulk sites for the W) are also reported. ΔE is in meV per Ni surface atom, Δx in Å, while $\Delta d_{n,n+1}$ is given in % of the bulk W-W interlayer spacing.

	H	T'		B
ΔE	3	0		359
	$\Delta d_{n,n+1}$	Δx	$\Delta d_{n,n+1}$	$\Delta d_{n,n+1}$
Ni	-18.9	0.26	-18.6	-11.4
W - 1 st	0.4	0.00	0.3	0.0
W - 2 nd	0.1	0.01	-0.1	0.0
W - 3 rd	0.1	0.01	0.0	0.0

3.2. 1×7 coincidence phase

The Ni/W(110) 1×7 structure is characterized by higher Ni density than the PS. As established experimentally [17], it has 9 Ni atoms per 7 substrate unit cells (the corresponding unit cell is illustrated in Fig. 2). The additional atoms are along the $[001]$ direction, while along $[1\bar{1}0]$ it remains pseudomorphic.

We obtained three different stable and meta-stable solutions depending on the initial configuration for the structural relaxation. They are shown in Fig. 2. Starting from an “ideal”, equidistant Ni-row arrangement along $[001]$ and $[1\bar{1}0]$, configuration C1 [Fig. 2 (a)] has been obtained. The C2 structure [Fig. 2 (b)] was obtained starting from several different initial structures, including the SXRD structure from [14]. The C3 structure [Fig. 2 (c)] resulted instead from a relaxation starting from a structure similar to the model superstructure of Ref. [14], but slightly less disordered, keeping only the distorted Ni hexagons. The C2 is the ground state, it is 196 meV and 244 meV per 1×1 W surface unit lower than the C3 and C1 configurations respectively.

The Ni layer in the C1 structure is very corrugated (with Ni sublayer separations, Δz , as large as 0.57 Å), as some of the Ni atoms sit on top of the underlying W atoms. The C2 structure [Fig. 2 (b) and atomic coordinates in Appendix] can be described by oscillating chains of Ni atoms, oriented parallel to the W $[001]$ direction, and with their axis projection on the W surface located mid-way between adjacent $[001]$ rows of W atoms. The Ni layer in the C2 structure is corrugated only slightly (Δz less than 0.15 Å) and is very similar to the bulk Ni(111) layer - same average nearest-neighbor (NN) distance of 2.51 Å, with a root-mean-square (rms) deviation of 0.12 Å,

and an angular rms deviation of 4.9° with respect to the average NN angle of 60° . The C3 structure, instead, as shown in Fig. 2 (c), has a more complicated structure, with distinct distorted Ni hexagons.

Based on SXRD measurements, Meyerheim et al. [14] proposed a rather disordered structure, characterized by distorted Ni hexagons and Ni atoms located mostly at or close to the bridge sites between W atoms. We note that C2 does not resemble it much. We find from our calculations that the bridge-site configuration is energetically very unfavorable. A possible explanation for the discrepancy between our theoretical structure and the SXRD-derived atomic structure is the coexistence of various phases with domain sizes of few nm [17, 16] observed under the growth conditions used in the SXRD measurement [14]. For such small domains, the structural relaxations at the domain boundaries are expected to be significant [43]. Furthermore, the coexistence of phases with similar periodicity, i.e. 1×8 and 1×7 phases, combined with the small domain sizes, possibly makes it difficult to distinguish the corresponding reciprocal-space features in the diffraction measurements. The disorder, which was essential in fitting the diffraction data in the mentioned SXRD study [14], is consistent with these observations. We note that such a disorder, resulting from room-temperature measurements, cannot be obtained from a coexistence of C1, C2 and C3 configurations due to the large energy differences between the C2 and the other two structures. However, we cannot exclude the possibility that the C2 structure could represent a better model to fit the SXRD data, as the study in [14] does not seem to take into account a C2-like structure in searching for the optimal fit.

Table 2. The first two interlayer distances for the 1×7 configurations, compared to the PS and clean W(110). The layer "0" refers to Ni.

	C1	C2	C3	PS	W
d ₀₁ (%)	-6.1	-10.1	-9.5	-18.6	
d ₁₂ (%)	1.1	0.0	0.5	0.3	-3.6

Our C2 structure, instead, corresponds to and is very much alike the theoretical model prediction of Ref. [34] for the 1×8 structure of Ni/Mo(110) and the experimental and theoretical 1×8 structure of Co/W(110) [46, 47]. In our case, the amplitude of the oscillations of the Ni chains is about 0.34 \AA . Mo and W are both bcc metals and have almost identical lattice parameters (the difference is about 0.6 %). Clearly, the model predictions for the Ni/Mo(110) are very relevant also for Ni/W(110), as our optimized structure demonstrates. Similarly, the nearest neighbor distances for bulk Ni and Co are very close ($\sim 0.5 \%$ difference), and one could expect some similarities of their adsorbate structures on W(110). Therefore, based on our results on Ni/W(110), one could expect that also the 1×7 phase of Co/W(110) should exist for coverages within the interval determined by the 1×1 and 1×8 phases.

In Table 2 we compare the first two average interlayer distances of the three 1×7

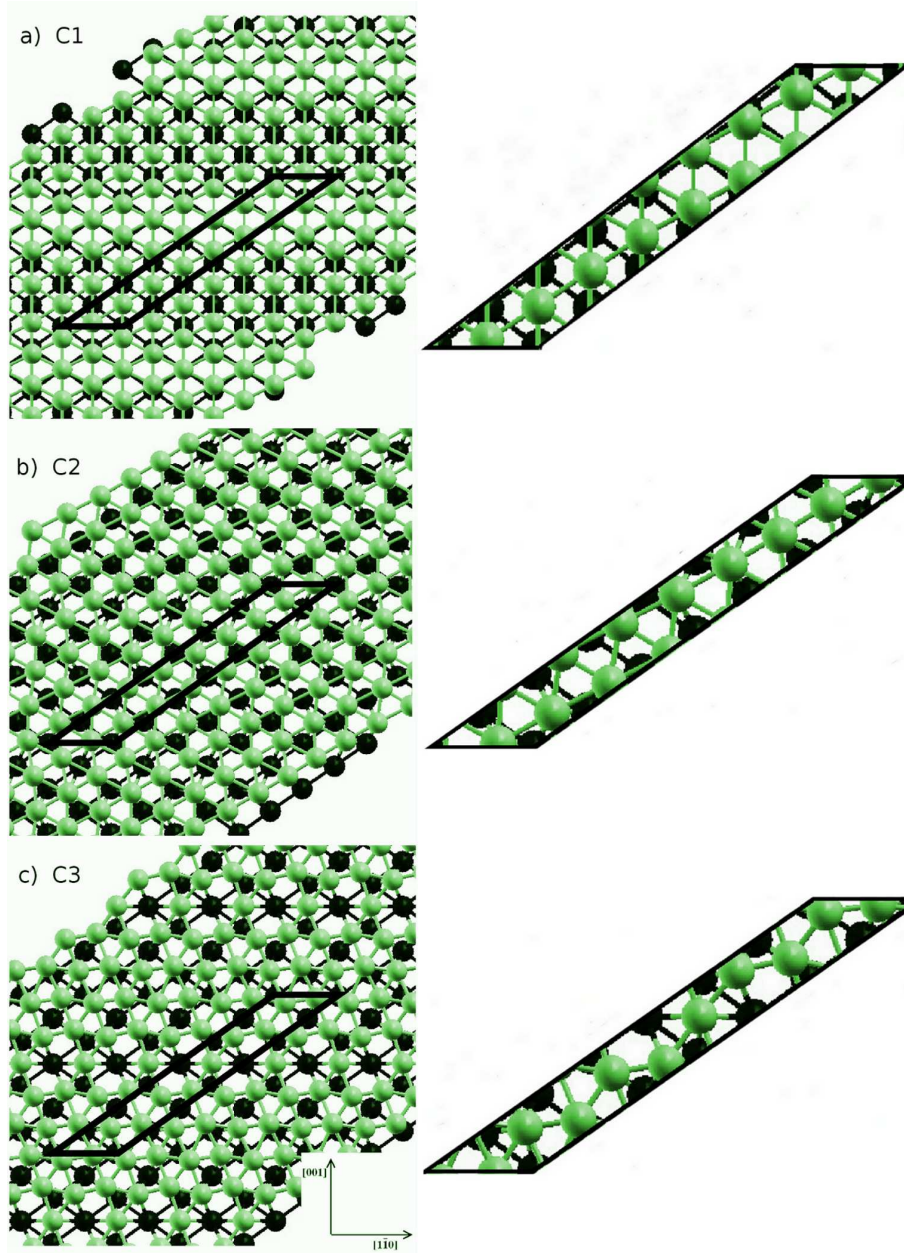


Figure 2. Relaxed 1×7 structures of Ni/W(110). Atomic colors and directions are like in Fig. 1. The surface unit cells are also indicated (thick black solid lines) and shown enlarged in the right column for each structure.

configurations with the PS and clean W(110) surface [48]. PS has the largest contraction of the first layer, roughly two times larger than the 1×7 configurations. Of those, C1's first layer is the least contracted due to the on-top position of the Ni atoms in a part of the surface unit cell. In all the 1×7 and 1×1 adsorbate structures considered, the W top-layer relaxation of -3.6% is removed. Only the C1 structure displays a non-negligible d_{12} relaxation, due to a relatively far top layer. We note that, although C2 and C3 have similar values for d_{01} , C2's interlayer spacing of 2.00 \AA is more similar

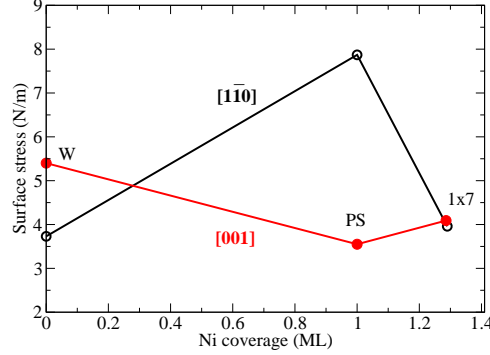


Figure 3. Evolution of the surface stress with Ni coverage, from the clean W(110) surface to the Ni/W(110) PS and 1×7 configurations. Open symbols, connected with a black line, denote stress along $[1\bar{1}0]$ and filled symbols, connected with a red (grey) line, along $[001]$. Lines are only guide to the eye.

(with less than 1 % difference) to the first layer spacing of the Ni(111) surface, which has a very small relaxation (we calculated it to be -0.4 %).

3.3. Surface stress

Table 3. Surface stress for the 1×1 structures characterized by different adsorption sites. All stresses are in N/m.

	H	T'	T	Q	B
$T_{[1\bar{1}0]}$	8.9	7.9	6.1	5.1	5.9
$T_{[001]}$	2.9	3.6	5.8	8.4	7.5

Table 4. Surface stress for the three 1×7 structures. All stresses are in N/m.

	$C1$	$C2$	$C3$
$T_{[1\bar{1}0]}$	9.5	4.0	0.2
$T_{[001]}$	2.7	4.1	3.5

In Fig. 3 we present the calculated surface stresses, along the $W[1\bar{1}0]$ and $W[001]$ directions, for the clean W(110) surface and for our ground-state PS and 1×7 Ni/W(110) surfaces [49]. They are displayed as a function of Ni coverage. The values for the clean W(110) surface are consistent with previous DFT values [43, 50].

A first observation is that the stresses are tensile (positive) for all the configurations, which means that the stress relaxation would cause contraction of interatomic distances

on the surface. This is not surprising, as tensile stress occurs at most metal surfaces, due to a charge redistribution upon bulk termination. From W to PS Ni/W the stress is increasing along $[1\bar{1}0]$, whereas it is decreasing along $[001]$, which is somewhat surprising. Considering the lattice mismatch, the Ni layer is under a strongly tensile (experimentally: 27 %, theoretically 30 %) epitaxial strain along $[001]$ (and experimentally under a 4 % strain, theoretically under a 6 % strain along $[1\bar{1}0]$). This would suggest a strongly tensile (positive), rather than compressive, change in the stress along $[001]$. In fact, the continuum elasticity estimates would yield tensile stresses along both directions [13, 14], with the stress along $[001]$ roughly two times larger.

Moreover, we notice a large change (decrease) in stress along $[1\bar{1}0]$ and almost no change along $[001]$ from the PS to the 1×7 configuration, although the change in strain (insertion of atoms, i.e., compressive change in strain) is occurring along $[001]$. In this case, the estimated change (decrease) of stress from the elasticity-theory model would be three times larger along $[001]$, than along $[1\bar{1}0]$ [10]. Similar surprising trends in the stress were detected experimentally [14]. In fact, there is a good general agreement between theory and experiment [13, 14]: most of the main features and changes of trends are reproduced, although our calculated change in the $[001]$ stress from clean W to PS (-2.0 N/m) is smaller in magnitude than the reported measured value in [13] (-2.9 N/m) and our $[001]$ stress change from clean W to 1×7 (-1.3 N/m) is larger/smaller in magnitude than the measured value reported in Ref. [13] (-0.8 N/m)/Ref. [14] (-2.1 N/m) [51]. It should be noted that different degrees of coexistence of Ni phases, other than the reference 1×7 phase, are likely to be responsible for the difference in the experimental values in [13] and [14].

In order to understand the influence of the surface structure on the stress in Fig. 3, we also evaluated the surface stress of the other PS and 1×7 structures we considered in the previous subsections. The results are reported in Table 3 (for the 1×1 structures) and 4 (for the 1×7 structures). The results for the 1×1 structure in Table 3 show that the Ni adsorption site has a critical influence on the surface stress. The H site (close to T') is characterized by an especially large stress (8.9 N/m) along $[1\bar{1}0]$ and low stress (2.9 N/m) along $[001]$, which account for the stress behaviour of the ground state (T') PS structure in Fig 3. The B site, instead, has a larger stress along $[001]$ (7.5 N/m) than along $[1\bar{1}0]$ (5.9 N/m), whereas the T site is characterized by a more isotropic ("averaged") stress (5.8 – 6.1 N/m). The stress is exactly isotropic somewhere off the T site, towards the Q site, which has reversed stresses, i.e., larger stress (8.4 N/m) is along $[001]$. At this site, along $[1\bar{1}0]$ the stress (5.1 N/m) is the smallest of all considered 1×1 structures, as it is steadily decreasing from the H site to the Q site.

Similar trends are observed for the 1×7 structure in Table 4, from which one can draw a relation between the stress of the predominant type of adsorption sites and the stress of the 1×7 structures. In particular, the C1 structure is characterized by an especially large stress (9.5 N/m) along $[1\bar{1}0]$ and low stress (2.7 N/m) along $[001]$. This is similar to the behaviour of the H structure, suggesting a dominant influence of the H site in determining the stress of the C1 structure. Similar to the T structure,

the C2 structure (including many Ni T-like sites) displays a nearly isotropic stress (4.0 – 4.1 N/m). This suggests a dominant influence, in this case, of T-like sites [Fig. 2 (b)] on the behaviour of the C2 stress. We also note that the C2 stress is somewhat lower than the T stress, which is consistent with a higher density (more compressed) Ni layer in the C2 structure, compared to the T structure. For the C3 structure, instead, the crucial element for the interpretation of the stress in Table 4 appears to be the presence of the 2 Ni atomic rows squeezed into one along $[1\bar{1}0]$, which causes compressive stress along $[1\bar{1}0]$.

We can apply the above findings towards an explanation of the anomalous trend (with respect to the expectations from the model elasticity theory) observed in Fig. 3 and in the experiment, from PS to 1×7 configurations. From elasticity theory, an essentially constant stress along $[1\bar{1}0]$ and a significant decrease of stress along $[001]$ are expected, while in both experiment and our calculations, we observe the opposite: there is a strong decrease along $[001]$ and a slight increase along $[1\bar{1}0]$. The observed trends can be rationalized, however, by considering the change in Ni adsorption sites, from H-like or T' site (i.e. essentially two-fold coordinated sites) in the PS configuration to mainly three-fold coordinated T-like sites in the C2 configuration. In fact, the results in Table 3 demonstrate a major influence of the type of site, occupied by the Ni, on the stress. They also indicate that the two-fold H-like sites tend to yield highly anisotropic stresses, with $T_{[1\bar{1}0]} \gg T_{[001]}$, whereas the three-fold T-like sites tend to produce an isotropic stress, whose value is equal to the average over the two perpendicular directions of the Ni stress components (for the same Ni density). On the basis of these considerations, the stress from PS to 1×7 is expected to increase along $[001]$ and decrease along $[1\bar{1}0]$, with the decrease being larger in magnitude, due to the effect of a larger Ni density in the 1×7 than in the PS case. We would like to emphasize that, in our case, unlike the case of alkali-metal adsorbates [12], the trends in the stress changes are not driven by a charge transfer effect. In fact, we evaluated the work function change (which is a measure of charge transfer) between the 1×1 and 1×7 phases. The work-function change between the T' 1×1 and C2 configurations is 0.2 eV. The small change of the work function, as calculated, indicates a very small charge transfer, which cannot explain the large change in stress when the Ni site changes [52].

Meyerheim et al. [14] also emphasized the importance of the W's 1st-layer displacement for their proposed structure, which had significant displacements of W atoms. We have checked the influence of the 1st W's layer on the surface stress in the C3 structure, the most disordered 1×7 structure we obtained theoretically. In the proposed structure based on the SXRD, the W in-plane displacements are extremely large, reaching even 0.5 Å. In our structure, the maximum displacements are about 10 times smaller. We fixed W positions in this layer to the ideal bulk positions, keeping the interlayer spacing unchanged. The stress of the C3 structure thus changed by only -0.4 N/m in both directions, indicating the W displacements are likely not the cause of the drastic stress change of the C3 structure with respect to PS, and instead it is likely that the influence of Ni atoms and their configuration is of the essential influence.

Finally, we note that the C2 structure may be defined with two harmonic functions, which describe the atomic displacements along $[1\bar{1}0]$ and $[001]$ [34], and create nearly regular hexagons. The resulting stress is actually almost isotropic, so one could hypothesize that although the system is not necessarily relaxing the surface stress, it is approaching the limit of a clean Ni surface. Even our calculated values are rather close, around 4 N/m for C2 and 3.5 N/m for the non-magnetic Ni(111). Therefore, it seems that in the case of the Ni/W(110) 1×7 reconstruction the minimum energy configuration coincides with highly isotropic arrangement of Ni atoms whose average stress also corresponds to the clean Ni(111) surface.

4. Conclusion

Motivated by puzzling measured stress changes in Ni/W(110), we performed a first-principles DFT study of the surface stress and structural properties of the PS and 1×7 coincidence phase. We determined the ground state 1×7 structure which is different than the one proposed based on SXRD. The latter structure is very irregular, with many distorted Ni hexagons, while ours includes a highly isotropic Ni(111)-like layer and can be described by oscillating Ni[001] chains with their axis projection on the W surface located mid-way between adjacent rows of [001] W atoms. The ground state 1×7 coincidence structure we obtain is, instead, similar to the model-theory prediction for the 1×8 Ni/Mo(110) structure and to the experimentally and theoretically described 1×8 phase of Co/W(110).

Furthermore, our calculated stresses qualitatively follow the measured stress changes with Ni coverage and reproduce the surprising trend of a larger stress change along the direction perpendicular to the Ni atomic density change. We explained the trends in the stress changes in terms of a dominant influence on stress of the Ni adsorption/coordination sites, as opposed to the interpretations based on the continuum elasticity theory or charge transfer. We expect our conclusions concerning the stress dependence on the adsorption/coordination sites to apply more generally to other related bimetallic systems involving transition-metal atoms.

Appendix A. 1×7 atomic positions

Here we list the atomic coordinates of the upper three layers for the lowest-energy 1×7 configuration, C2.

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Table A1. Atomic positions in Å for the upper three layers for 1×7 . x is along $[\bar{1}10]$ and y along $[001]$.

	x	y	z		x	y	z		x	y	z
Ni ₁	16.86	10.68	24.12	W ₁	19.92	10.99	22.14	W ₈	2.20	0.00	19.92
Ni ₂	3.38	0.89	24.20	W ₂	2.20	1.57	22.18	W ₉	4.42	1.57	19.93
Ni ₃	5.35	2.15	24.17	W ₃	4.44	3.14	22.12	W ₁₀	6.65	3.14	19.91
Ni ₄	5.17	4.60	24.06	W ₄	6.66	4.70	22.11	W ₁₁	8.87	4.71	19.91
Ni ₅	7.41	3.35	24.08	W ₅	8.86	6.28	22.17	W ₁₂	11.08	6.28	19.92
Ni ₆	11.95	5.81	24.15	W ₆	11.05	7.84	22.16	W ₁₃	13.26	7.85	19.92
Ni ₇	9.96	7.03	24.21	W ₇	13.26	9.42	22.12	W ₁₄	15.51	9.42	19.92
Ni ₈	12.40	8.25	24.14								
Ni ₉	14.72	9.44	24.08								

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- [52] We also evaluated the work function change between the clean W(110) and 1×1 phases: the change is -0.4 eV for the T' and H sites and -0.6 eV for the B site. This is almost identical to the previous LDA [54] and GGA [42] findings and somewhat different (by 0.3-0.4 eV in magnitude) from the experimental value [18]. However, from both theoretical and experimental value of the work-function change, which is considerably smaller in magnitude than for Li/Mo(110) [12], one can deduce that the charge transfer is not responsible for the drastic surface-stress changes.
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